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RESEARCH MEMORANDUM

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## RESEARCH MEMORANDUM

ADDITIONAL VALUES FOR THE EQUILIBRIUM COMPOSITION  
AND THERMODYNAMIC PROPERTIES OF AIR

F. R. Gilmore

RM-2328

December 30, 1959

Assigned to. \_\_\_\_\_

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#### SUMMARY

Supplementing RM-1543, values of the equilibrium composition and thermodynamic properties of air are presented at two additional temperatures, 10,000 and 50,000°K. The pure ideal-gas properties needed for these calculations are included. Equilibrium values for the principal charged particles at 1000 and 2000°K, and for the CN molecule between 1000 and 8000°K are also listed. Finally, the thermodynamic properties of air between 1000 and 10,000°K at high densities (10 to 316 times standard density) are tabulated. These properties are calculated to include approximate corrections for the intermolecular interactions.

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## INTRODUCTION AND DISCUSSION

Tables of the equilibrium composition and thermodynamic properties of air for eleven temperatures between 1000 and 24,000 °K and eight densities between  $10^{-6}$  and 10 times standard density were presented several years ago in RM-1543.<sup>(1)</sup> Since that time Hilsenrath and Beckett of the Bureau of Standards have published more complete tables of thermodynamic properties<sup>(2,3)</sup> covering a wider range of temperatures and densities with many more intermediate points. However, they have not published the equilibrium composition values obtained in their work; moreover, these values, even if published, would not satisfy all practical needs because of omission of carbon compounds and argon in the calculations. Consequently, as various practical problems involving the equilibrium air composition have arisen, calculations supplementing those of RM-1543 have been made. The results are collected in the present memorandum. In addition, neither the RAND nor the Bureau of Standards thermodynamic calculations included corrections for gas imperfection due to forces between the molecules, which are significant at the higher air densities. The results of some corrected calculations are reported herein.

Tables 1 to 5 supplement RM-1543 by presenting data for two additional temperatures, 10,000 and 50,000 °K. The pure ideal gas properties listed in Tables 1 and 2 were calculated using the same methods and spectroscopic data as in the earlier work.<sup>(1)</sup> These values were then used to compute the equilibrium composition, Tables 3 and 4. The equilibrium thermodynamic properties were calculated for 10,000 °K (Table 5) but not for 50,000 °K, since the values in Ref. 3 should be accurate for the latter temperature.

The tabulated values for pressure, entropy, and number of moles per mole of cold air at 10,000 °K agree reasonably well with the values of Hilsenrath and Beckett,<sup>(2)</sup> considering the neglect of argon in the latter calculations. For the energy, however, there are differences of 7, 2 and 6 per cent at  $\rho/\rho_0 = 10, 1$  and  $10^{-6}$ , respectively, while the agreement at other densities is within 1 per cent. These differences are quite surprising because no such differences were found at 8000 or 12,000 °K.<sup>(1)</sup> The calculations for the three points in question were rechecked, but no error was found.

In RM-1543 the equilibrium amounts of charged particles at 1000 and 2000 °K were not calculated, since they comprise less than one-billionth of the total particles. However, there is some interest in the charged particles, since even a very tiny fraction can affect the propagation of radio waves. The results of calculations are given in Table 6. As indicated on the table, some of the results are sensitive to the value assumed for the electron affinity of  $O_2$ , which is still uncertain experimentally. Consequently, Table 6 contains two values for each quantity, corresponding to two possible values, 1.0 and 0.8 ev, for the affinity.<sup>(4)</sup> Recently, papers indicating that this affinity may be as low as 0.15 ev have been published,<sup>(5,6)</sup> although the present writer favors a value larger than 0.4 ev, for reasons which will be published later. In addition to this uncertainty, it should be noted that the presence of even a few parts per million of an easily ionizable substance can increase the number of free electrons by several orders of magnitude at these temperatures.

The values listed in Table 6 for an affinity of 1 ev agree within 10 per cent with values given in a recent Douglas Aircraft Report,<sup>(7)</sup> except for obvious errors in the latter values for  $O^-$  at 1000 °K and



$\rho/\rho_0 = 1$  and  $10^{-1}$ , and at 2000 °K and  $\rho/\rho_0 = 1$  and  $10^{-2}$ .

The molecule CN is present in such small amounts in equilibrium air that it was omitted in the calculations of RM-1543. However, it is such an efficient radiator of visible light that it makes a significant contribution to the total radiation from air over a considerable range of temperatures and densities.<sup>(8)</sup> For this reason, equilibrium values for CN in air between 1000 and 8000 °K have been calculated, and are presented in Table 7. These results are based on ideal-gas free energy values of Johnston, Belzer and Savedoff<sup>(9)</sup> (extrapolated for temperatures above 6000 °K), and a dissociation energy  $D(\text{CN}) = 7.59 \pm 0.09$  ev obtained recently by Knight and Rink.<sup>(10)</sup> Although it was found very recently that the evidence for this value is not as conclusive as previously supposed, it still appears to be the most probable value.<sup>(11)</sup>

Neither the RAND<sup>(1)</sup> nor the Bureau of Standards<sup>(2,3)</sup> thermodynamic calculations include corrections for gas imperfection, which typically amount to about 1 per cent at  $\rho/\rho_0 = 10$ , and 10 per cent at  $\rho/\rho_0 = 100$ . To make such corrections accurately at high temperatures, one needs information not only on the familiar interactions between ground-state molecules, but also on the interactions between excited molecules, atoms and ions. Knowledge of the latter is far from complete, although several papers on this question have recently been published. Fortunately, at high densities the degree of dissociation is moderately small and the degree of ionization quite small up to about 10,000 °K. Moreover, the fraction of excited molecules is small,<sup>(1)</sup> except for the lowest excited state of  $\text{O}_2$ , which has an interatomic distance and other properties nearly the same as the ground state. Also, the fraction of NO does not exceed 10 per cent and

its interaction energy is not greatly different from that of  $N_2$  or  $O_2$ . Thus, it is reasonable to use a mean intermolecular potential for "air" molecules derived from measured second virial coefficients and represented by a Lennard-Jones 6-12 potential with constants  $\epsilon/k = 102^\circ K$  and  $\sigma = 3.62 \text{ \AA}$ .<sup>(12)</sup> Existing tables and formulas<sup>(12)</sup> can then be used to calculate the second and third virial coefficients and the corresponding corrections to the pressure, energy and entropy, for all temperatures for which the assumptions discussed above are reasonable.

The results of such calculations, with the additional assumption that the intermolecular forces do not change the chemical equilibrium constants significantly, are presented in Table 8 for temperatures between 2000 and 10,000  $^\circ K$  and density ratios between 10 and 316. For the highest density considered the corrections to the pressure (and to  $Z = PV/RT$ ) are roughly 50 per cent, and the accuracy of the tabulated values of  $P$  and  $Z$  is estimated to be within 10 per cent. Corrections to the energy and enthalpy are only a few per cent at  $\rho/\rho_0 = 316$ , while corrections to the entropy are almost negligible; the probable errors in these quantities are correspondingly smaller. All corrections vary approximately in direct proportion to the density, so that at  $\rho/\rho_0 = 10$  even the pressure should be accurate to better than 1 per cent. The significant differences between the values of Table 8 and the values of Hilsenrath and Beckett<sup>(2)</sup> are due almost entirely to the corrections for gas imperfection, except at 10,000  $^\circ K$ , where the discrepancies already mentioned in connection with Table 5 show up even more prominently at the higher densities. The reason for these discrepancies is not known.

Table 1

Ideal Gas Internal Energies and Free Energies at 10,000 °K.

Species	$\frac{E^{\circ} - E_{\circ}^{\circ}}{RT}$	$-\frac{F^{\circ} - E_{\circ}^{\circ}}{RT}$
NO <sub>2</sub>	*	44.13
CO	3.55	33.965
CO <sup>+</sup>	3.92	34.777
N <sub>2</sub>	3.52	33.147
N <sub>2</sub> <sup>+</sup>	4.19	34.560
NO	3.54	35.776
NO <sup>+</sup>	3.61	34.015
O <sub>2</sub> <sup>-</sup>	4.48	36.221
O <sub>2</sub>	4.01	35.470
O <sub>2</sub> <sup>+</sup>	3.87	35.225
e <sup>-</sup>	1.5000	8.7917
C	1.7088	25.4124
C <sup>+</sup>	1.5319	24.8792
N	1.9522	24.8728
N <sup>+</sup>	1.6493	25.5664
N <sup>++</sup>	1.5210	25.0957
N <sup>+++</sup>	1.5055	23.3206
O <sup>-</sup>	1.5000	25.3114
O	1.6385	25.7623
O <sup>+</sup>	1.7170	24.9615
O <sup>++</sup>	1.6186	25.7177
O <sup>+++</sup>	1.5371	25.2746
Ne	1.5000	23.8630
Ne <sup>+</sup>	1.5348	25.6236
A	1.5005	24.8920
A <sup>+</sup>	1.5596	26.6196
A <sup>++</sup>	1.7184	27.0923

\* Not calculated.

Table 2

Ideal Gas Internal Energies and Free Energies at 50,000 °K ( $kT = 4.31$  ev).

Species	$\frac{E^0 - E_0^0}{RT}$	$-\frac{F^0 - E_0^0}{RT}$
$e^-$	1.5000	12.8153
N	3.5604	30.8844
$N^+$	2.3869	30.1583
$N^{++}$	2.2220	29.5472
$N^{+++}$	2.8057	28.2394
O	3.0909	30.8530
$O^+$	2.3800	29.9746
$O^{++}$	1.9616	30.1529
$O^{+++}$	2.0763	29.5995
A	4.3846	31.1528
$A^+$	2.9268	31.1016
$A^{++}$	2.2133	31.5795

Values for the neutral species are quite approximate, because of the  
 arbitrary electronic cutoff (see FM-1543).

Table 3

Equilibrium Composition of Dry Air at 10,000 °K\*

UNITS: Particles per Air Atom (Multiply by 1.9910 to get Moles per Mole of Air)

Particle	Density Ratio $\rho/\rho_0$							
	10	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
NO <sub>2</sub>	$3.22^{-6}$	$8.31^{-8}$	$1.16^{-9}$	$1.17^{-11}$	$1.01^{-13}$	$6.22^{-16}$	$1.31^{-18}$	$2.31^{-22}$
CO	$1.03^{-4}$	$2.58^{-5}$	$2.85^{-6}$	$2.29^{-7}$	$1.33^{-8}$	$4.78^{-10}$	$8.13^{-12}$	$3.63^{-14}$
CO <sup>+</sup>	$1.66^{-7}$	$1.58^{-7}$	$5.72^{-8}$	$1.47^{-8}$	$2.78^{-9}$	$3.48^{-10}$	$2.51^{-11}$	$7.18^{-13}$
N <sub>2</sub>	$2.51^{-1}$	$1.13^{-1}$	$2.02^{-2}$	$2.14^{-3}$	$1.90^{-4}$	$1.27^{-5}$	$3.78^{-7}$	$2.12^{-9}$
N <sub>2</sub> <sup>+</sup>	$1.29^{-4}$	$2.21^{-4}$	$1.29^{-4}$	$4.37^{-5}$	$1.26^{-5}$	$2.94^{-6}$	$3.71^{-7}$	$1.33^{-8}$
NO	$2.35^{-2}$	$5.49^{-3}$	$7.49^{-4}$	$7.64^{-5}$	$6.89^{-6}$	$4.89^{-7}$	$1.66^{-8}$	$1.07^{-10}$
NO <sup>+</sup>	$7.46^{-4}$	$6.61^{-4}$	$2.95^{-4}$	$9.65^{-5}$	$2.83^{-5}$	$6.99^{-6}$	$1.01^{-6}$	$4.15^{-8}$
O <sub>2</sub>	$8.24^{-7}$	$2.64^{-8}$	$8.41^{-10}$	$2.59^{-11}$	$7.26^{-13}$	$1.58^{-14}$	$1.44^{-16}$	$1.67^{-19}$
O <sub>2</sub> <sup>+</sup>	$1.01^{-3}$	$1.23^{-4}$	$1.28^{-5}$	$1.26^{-6}$	$1.15^{-7}$	$8.70^{-9}$	$3.37^{-10}$	$2.51^{-12}$
O <sub>2</sub> <sup>++</sup>	$4.36^{-6}$	$2.02^{-6}$	$6.88^{-7}$	$2.17^{-7}$	$6.42^{-8}$	$1.69^{-8}$	$2.78^{-9}$	$1.33^{-10}$
e <sup>-</sup>	$1.09^{-3}$	$2.87^{-3}$	$8.77^{-3}$	$2.74^{-2}$	$8.43^{-2}$	$2.42^{-1}$	$5.71^{-1}$	$8.90^{-1}$
C	$5.74^{-5}$	$1.29^{-4}$	$1.40^{-4}$	$1.14^{-4}$	$6.91^{-5}$	$2.86^{-5}$	$7.83^{-6}$	$1.28^{-6}$
C <sup>+</sup>	$5.85^{-7}$	$5.01^{-6}$	$1.77^{-5}$	$4.61^{-5}$	$9.10^{-5}$	$1.31^{-4}$	$1.52^{-4}$	$1.57^{-4}$
N	$2.59^{-1}$	$5.49^{-1}$	$7.35^{-1}$	$7.56^{-1}$	$7.13^{-1}$	$5.82^{-1}$	$3.18^{-1}$	$1.52^{-2}$
N <sup>+</sup>	$1.99^{-4}$	$1.60^{-3}$	$7.03^{-3}$	$2.31^{-2}$	$7.10^{-2}$	$2.02^{-1}$	$4.66^{-1}$	$7.09^{-1}$
N <sup>++</sup>	$1.22^{-15}$	$3.73^{-14}$	$5.37^{-13}$	$5.65^{-12}$	$5.64^{-11}$	$5.59^{-10}$	$5.47^{-9}$	$5.34^{-8}$
N <sup>+++</sup>	$2.11^{-36}$	$2.45^{-34}$	$1.15^{-32}$	$3.88^{-31}$	$1.26^{-29}$	$4.35^{-28}$	$1.80^{-26}$	$1.13^{-24}$
O <sup>-</sup>	$7.66^{-5}$	$2.23^{-5}$	$6.97^{-6}$	$2.16^{-6}$	$6.34^{-7}$	$1.58^{-7}$	$2.32^{-8}$	$9.88^{-10}$
O	$1.85^{-1}$	$2.05^{-1}$	$2.09^{-1}$	$2.07^{-1}$	$1.98^{-1}$	$1.72^{-1}$	$1.07^{-1}$	$2.92^{-2}$
O <sup>+</sup>	$9.42^{-5}$	$3.96^{-4}$	$1.32^{-3}$	$4.19^{-3}$	$1.30^{-2}$	$3.94^{-2}$	$1.01^{-1}$	$1.82^{-1}$
O <sup>++</sup>	$3.18^{-18}$	$5.08^{-17}$	$5.54^{-16}$	$5.63^{-15}$	$5.67^{-14}$	$5.99^{-13}$	$6.70^{-12}$	$7.51^{-11}$
O <sup>+++</sup>	$3.42^{-42}$	$2.07^{-40}$	$7.10^{-39}$	$2.41^{-37}$	$7.88^{-36}$	$2.90^{-34}$	$1.37^{-32}$	$9.89^{-31}$
Ne	$2.00^{-5}$	$2.00^{-5}$	$2.00^{-5}$	$2.00^{-5}$	$2.00^{-5}$	$2.00^{-5}$	$2.00^{-5}$	$1.98^{-5}$
Ne <sup>+</sup>	$1.30^{-11}$	$4.93^{-11}$	$1.41^{-10}$	$5.16^{-10}$	$1.68^{-9}$	$5.84^{-9}$	$2.48^{-8}$	$1.57^{-7}$
A	$4.69^{-3}$	$4.69^{-3}$	$4.68^{-3}$	$4.65^{-3}$	$4.57^{-3}$	$4.30^{-3}$	$3.42^{-3}$	$1.38^{-3}$
A <sup>+</sup>	$9.17^{-7}$	$3.47^{-6}$	$1.14^{-5}$	$3.62^{-5}$	$1.16^{-4}$	$3.78^{-4}$	$1.28^{-3}$	$3.30^{-3}$
A <sup>++</sup>	$1.45^{-16}$	$2.09^{-15}$	$2.24^{-14}$	$2.28^{-13}$	$2.37^{-12}$	$2.70^{-11}$	$3.87^{-10}$	$6.40^{-9}$

\* For all values, the power of ten is indicated by a superscript. The standard density is  $\rho_0 = 1.2931 \times 10^{-3} \text{ gm/cm}^3$  (corresponding to 1 atm. pressure at 273.16 °K).

Table 4

Equilibrium Composition of Dry Air at 50,000 °K.

UNITS: Particles per Air Atom (Multiply by 1.991 to get Moles per Mole of Air)\*

Particle	Density Ratio $\rho/\rho_0$							
	10	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
$e^-$	$7.53^{-1}$	$1.23^0$	$1.76^0$	$2.11^0$	$2.58^0$	$2.92^0$	$2.99^0$	$3.00^0$
N	$2.32^{-1}$	$3.76^{-2}$	$1.91^{-3}$	$2.95^{-5}$	$2.00^{-7}$	$4.30^{-10}$	$4.88^{-13}$	$4.94^{-16}$
$N^+$	$5.14^{-1}$	$5.10^{-1}$	$1.81^{-1}$	$2.33^{-2}$	$1.29^{-3}$	$2.45^{-5}$	$2.72^{-7}$	$2.75^{-9}$
$N^{++}$	$3.87^{-2}$	$2.35^{-1}$	$5.86^{-1}$	$6.27^{-1}$	$2.84^{-1}$	$4.77^{-2}$	$5.16^{-3}$	$5.21^{-4}$
$N^{+++}$	$2.31^{-5}$	$8.62^{-4}$	$1.50^{-2}$	$1.34^{-1}$	$4.98^{-1}$	$7.36^{-1}$	$7.79^{-1}$	$7.84^{-1}$
O	$6.08^{-2}$	$1.08^{-2}$	$6.96^{-4}$	$1.34^{-5}$	$1.38^{-7}$	$4.35^{-10}$	$5.39^{-13}$	$5.50^{-16}$
$O^+$	$1.44^{-1}$	$1.56^{-1}$	$7.05^{-2}$	$1.13^{-2}$	$9.49^{-4}$	$2.64^{-5}$	$3.20^{-7}$	$3.26^{-9}$
$O^{++}$	$6.58^{-3}$	$4.38^{-2}$	$1.38^{-1}$	$1.85^{-1}$	$1.27^{-1}$	$3.12^{-2}$	$3.69^{-3}$	$3.76^{-4}$
$O^{+++}$	$1.47^{-6}$	$5.99^{-5}$	$1.33^{-3}$	$1.47^{-2}$	$8.29^{-2}$	$1.80^{-1}$	$2.07^{-1}$	$2.11^{-1}$
A	$8.62^{-4}$	$7.25^{-5}$	$2.06^{-6}$	$3.14^{-8}$	$4.71^{-10}$	$6.07^{-12}$	$6.35^{-14}$	$6.35^{-16}$
$A^+$	$2.83^{-3}$	$1.46^{-3}$	$2.89^{-4}$	$3.68^{-5}$	$4.52^{-6}$	$5.13^{-7}$	$5.25^{-8}$	$5.25^{-9}$
$A^{++}$	$1.00^{-3}$	$3.16^{-3}$	$4.40^{-3}$	$4.65^{-3}$	$4.69^{-3}$	$4.69^{-3}$	$4.69^{-3}$	$4.69^{-3}$

\* For all values, the power of ten is indicated by a superscript.

Table 5  
Thermodynamic Properties of Air at 10,000 °K

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Density Ratio $\rho/\rho_0$							
10	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
<u>Pressure, Atmospheres</u>							
5.296 <sup>+2</sup>	6.423 <sup>+1</sup>	7.181 <sup>0</sup>	7.485 <sup>-1</sup>	7.902 <sup>-2</sup>	9.055 <sup>-3</sup>	1.144 <sup>-3</sup>	1.378 <sup>-4</sup>
<u>Pressure, Dynes Per Square Centimeter</u>							
5.366 <sup>+8</sup>	6.508 <sup>+7</sup>	7.276 <sup>+6</sup>	7.584 <sup>+5</sup>	8.006 <sup>+4</sup>	9.175 <sup>+3</sup>	1.159 <sup>+3</sup>	1.396 <sup>+2</sup>
<u>Internal Energy, <math>E - E_0</math>, Calories Per Gram</u>							
5.589 <sup>+3</sup>	7.829 <sup>+3</sup>	9.398 <sup>+3</sup>	1.013 <sup>+4</sup>	1.156 <sup>+4</sup>	1.543 <sup>+4</sup>	2.352 <sup>+4</sup>	2.978 <sup>+4</sup>
<u>Internal Energy, <math>E - E_0</math>, Electron Volts Per Atom</u>							
3.526 <sup>0</sup>	4.939 <sup>0</sup>	5.929 <sup>0</sup>	6.393 <sup>0</sup>	7.296 <sup>0</sup>	9.737 <sup>0</sup>	1.484 <sup>+1</sup>	1.878 <sup>+1</sup>
<u>Internal Energy Density, <math>(E - E_0)\rho</math>, Ergs Per Cubic Centimeter</u>							
3.024 <sup>+9</sup>	4.236 <sup>+8</sup>	5.085 <sup>+7</sup>	5.482 <sup>+6</sup>	6.257 <sup>+5</sup>	8.350 <sup>+4</sup>	1.273 <sup>+4</sup>	1.611 <sup>+3</sup>
<u>Dimensionless Internal Energy, <math>(E - E_0)/RT</math> (Per Initial Mole of Air)</u>							
8.147 <sup>0</sup>	1.141 <sup>+1</sup>	1.370 <sup>+1</sup>	1.477 <sup>+1</sup>	1.686 <sup>+1</sup>	2.250 <sup>+1</sup>	3.429 <sup>+1</sup>	4.340 <sup>+1</sup>
<u>Entropy of Dry Air in Chemical Equilibrium, <math>S/R</math> Per Mole of Cold Air</u>							
3.868 <sup>+1</sup>	4.574 <sup>+1</sup>	5.264 <sup>+1</sup>	5.839 <sup>+1</sup>	6.530 <sup>+1</sup>	7.622 <sup>+1</sup>	9.365 <sup>+1</sup>	1.138 <sup>+2</sup>
<u>Number of Moles Per Mole of Cold Air</u>							
1.445 <sup>0</sup>	1.758 <sup>0</sup>	1.966 <sup>0</sup>	2.041 <sup>0</sup>	2.158 <sup>0</sup>	2.473 <sup>0</sup>	3.128 <sup>0</sup>	3.763 <sup>0</sup>
<u>Effective Specific Heat Ratio for Shock Waves, <math>\gamma' = 1 + P/\rho E</math></u>							
1.1773 <sup>0</sup>	1.1541 <sup>0</sup>	1.1435 <sup>0</sup>	1.1382 <sup>0</sup>	1.1280 <sup>0</sup>	1.1099 <sup>0</sup>	1.09123 <sup>0</sup>	1.08670 <sup>0</sup>

Note: For all values, the power of ten is indicated by a superscript.

Table 6

Equilibrium Composition of Dry Air: Charged Particles

UNITS: Particles per Air Atom (Multiply by 1.9910 to get Moles per Mole of Air)

Temperature  $T = 1000^{\circ}\text{K}$

Particle	Density Ratio $\rho/\rho_0$							
	10	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
$\text{NO}^+$	$13.8-7.1^{-25}$	$13.8-7.1^{-25}$	$13.8-7.2^{-25}$	$13.9-7.3^{-25}$	$14.8-8.9^{-25}$	$2.2-1.8^{-24}$	$5.4-5.3^{-24}$	$1.7-1.7^{-23}$
$\text{O}_2^-$	$13.8-7.1^{-25}$	$13.8-7.1^{-25}$	$13.8-7.1^{-25}$	$13.7-7.0^{-25}$	$12.9-5.7^{-25}$	$8.8-2.8^{-25}$	$35.1-9.6^{-26}$	$11.4-3.1^{-26}$
$e^-$	$2.0-3.9^{-29}$	$2.0-3.9^{-28}$	$2.0-3.9^{-27}$	$2.0-3.9^{-26}$	$1.9-3.1^{-25}$	$1.3-1.5^{-24}$	$5.1-5.2^{-24}$	$1.7-1.7^{-23}$
$\text{O}^-$	$6.3-12.1^{-33}$	$2.0-3.9^{-32}$	$6.3-12.1^{-32}$	$2.0-3.8^{-31}$	$5.8-9.8^{-31}$	$1.3-1.5^{-30}$	$1.6-1.6^{-30}$	$1.6-1.6^{-30}$

Temperature  $T = 2000^{\circ}\text{K}$ 

$\text{NO}^+$	$5.1-2.9^{-13}$	$5.4-3.4^{-13}$	$7.7-6.5^{-13}$	$1.9-1.9^{-12}$	$5.8-5.8^{-12}$	$1.8-1.8^{-11}$	$5.7-5.7^{-11}$	$1.7-1.7^{-10}$
$\text{O}_2^-$	$5.0-2.8^{-13}$	$4.8-2.4^{-13}$	$3.3-1.3^{-13}$	$13.5-4.4^{-14}$	$4.4-1.4^{-14}$	$13.5-4.2^{-15}$	$4.0-1.3^{-15}$	$10.1-3.2^{-16}$
$\text{e}^-$	$6.6-11.5^{-15}$	$6.2-9.9^{-14}$	$4.3-5.2^{-13}$	$1.8-1.8^{-12}$	$5.8-5.8^{-12}$	$1.8-1.8^{-11}$	$5.7-5.7^{-11}$	$1.7-1.7^{-10}$
$\text{O}^-$	$4.6-8.0^{-16}$	$1.4-2.2^{-15}$	$3.0-3.6^{-15}$	$4.0-4.0^{-15}$	$4.0-4.0^{-15}$	$3.9-3.9^{-15}$	$3.8-3.8^{-15}$	$3.3-3.3^{-15}$

Explanatory Note: The amount of  $O_2^-$  at all densities, and the amounts of  $NO^+$ ,  $e^-$  and  $O^-$  at the higher densities are quite sensitive to the electron affinity of  $O_2$ . The best value for EA ( $O_2$ ) is probably  $0.9 \pm 0.1$  eV, <sup>(4)</sup> although there is some evidence that it may be smaller. <sup>(5,6)</sup> The table above contains two entries for each quantity. The first corresponds to the upper limit EA ( $O_2$ ) = 1.0 eV (consistent with RM-1543); the second corresponds to the lower limit EA ( $O_2$ ) = 0.8 eV. The power of ten is indicated by a superscript; it is the same for each pair.



Table 7  
Number of Molecules of CN per Air Atom\*  
(Multiply by 1.991 to get Moles per Mole of Air)

Temperature °K	Density Ratio $\rho/\rho_0$							
	10	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
1000	$1.05^{-43}$	$3.32^{-43}$	$1.05^{-42}$	$3.32^{-42}$	$1.05^{-41}$	$3.32^{-41}$	$1.05^{-40}$	$3.32^{-40}$
2000	$9.27^{-22}$	$2.95^{-21}$	$9.22^{-21}$	$2.92^{-20}$	$9.01^{-20}$	$2.73^{-19}$	$7.43^{-19}$	$1.73^{-18}$
3000	$1.70^{-14}$	$4.74^{-14}$	$1.11^{-13}$	$2.08^{-13}$	$3.75^{-13}$	$8.88^{-13}$	$2.63^{-12}$	$8.20^{-12}$
4000	$4.63^{-11}$	$8.15^{-11}$	$1.45^{-10}$	$3.45^{-10}$	$1.01^{-9}$	$3.11^{-9}$	$9.51^{-9}$	$2.69^{-8}$
5000	$3.40^{-9}$	$6.14^{-9}$	$1.51^{-8}$	$4.42^{-8}$	$1.29^{-7}$	$3.13^{-7}$	$3.05^{-7}$	$5.66^{-8}$
6000	$6.18^{-8}$	$1.40^{-7}$	$3.82^{-7}$	$9.79^{-7}$	$1.26^{-6}$	$3.39^{-7}$	$3.44^{-8}$	$2.39^{-9}$
7000	$5.80^{-7}$	$1.42^{-6}$	$3.16^{-6}$	$2.67^{-6}$	$4.94^{-7}$	$4.37^{-8}$	$2.66^{-9}$	$1.13^{-10}$
8000	$3.09^{-6}$	$6.49^{-6}$	$5.65^{-6}$	$1.13^{-6}$	$1.05^{-7}$	$6.70^{-9}$	$2.88^{-10}$	$7.93^{-11}$

\* For each value, the power of ten is indicated by a superscript. These values are based on  $D(\text{CN}) = 7.59 \pm 0.09 \text{ ev.}^{(10)}$

Table 8  
Thermodynamic Properties of High-Density Air\*

$\log \rho/\rho_0$	$Z = PV/RT$	$E/RT$	$H/RT$	$S/R$	$10^n \frac{P}{\text{atm}}$	$n$
<u>2000 °K</u>						
2.5	1.610	2.980	4.590	23.51	3.728	3
2.0	1.154	2.956	4.110	24.66	8.448	2
1.5	1.045	2.958	4.003	25.82	2.418	2
1.0	1.014	2.960	3.974	26.98	7.421	1
<u>3000 °K</u>						
2.5	1.613	3.315	4.928	25.18	5.602	3
2.0	1.161	3.282	4.443	26.32	1.275	3
1.5	1.050	3.289	4.339	27.48	3.645	2
1.0	1.017	3.303	4.320	28.58	1.117	2
<u>4000 °K</u>						
2.5	1.599	3.636	5.235	26.49	7.403	3
2.0	1.164	3.590	4.754	27.59	1.704	3
1.5	1.060	3.673	4.733	28.83	4.908	2
1.0	1.037	3.798	4.835	30.08	1.518	2
<u>5000 °K</u>						
2.5	1.592	3.871	5.463	27.46	9.200	3
2.0	1.182	3.916	5.098	28.72	2.163	3
1.5	1.092	4.102	5.194	30.28	6.319	2
1.0	1.088	4.381	5.469	31.60	1.993	2
<u>6000 °K</u>						
2.5	1.606	4.091	5.697	28.38	1.115	4
2.0	1.212	4.212	5.424	29.53	2.663	3
1.5	1.137	4.472	5.609	31.20	7.895	2
1.0	1.142	4.800	5.942	32.85	2.510	2
<u>7000 °K</u>						
2.5	1.628	4.280	5.908	29.20	1.319	4
2.0	1.250	4.459	5.709	30.66	3.202	3
1.5	1.180	4.759	5.939	32.14	9.551	2
1.0	1.191	5.147	6.338	33.95	3.055	2

Table 8 (continued)  
Thermodynamic Properties of High-Density Air\*

$\log \rho/\rho_0$	$Z = PV/RT$	$E/RT$	$H/RT$	$S/R$	$10^n P$ atm	$n$
<u>8000 °K</u>						
2.5	1.660	4.476	6.136	29.90	1.536	4
2.0	1.289	4.722	6.011	31.42	3.776	3
1.5	1.235	5.148	6.383	33.30	1.143	3
1.0	1.255	5.696	6.951	35.22	3.676	2
<u>10,000 °K</u>						
2.5	1.737	5.648	7.385	31.58	2.010	4
2.0	1.397	6.148	7.545	33.45	5.114	3
1.5	1.376	6.950	8.326	35.69	1.593	3
1.0	1.466	8.149	9.615	38.68	5.365	2

\* Includes correction for gas imperfection using second and third virial coefficients based on the Lennard-Jones potential for "air" molecules. (12)  
Although quite crude at the higher temperatures where deviations from the Lennard-Jones potential become significant and also where there is considerable dissociation, this correction should still be of the right order of magnitude.

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